

DOPED LiMn_2O_4 WITH Ti AND Sn AS CATHODE FOR Li-ION BATTERY

*Aida Fazliza Mat Fadzil¹, Norlida Kamarulzaman¹, Mohd Azmi Bustam²

¹Centre for Nanomaterials Research
Institute of Science
Universiti Teknologi MARA
40450 Shah Alam, Selangor, Malaysia

²Chemical Engineering Department
University Teknologi PETRONAS
Seri Iskandar,
32610 Tronoh, Perak, Malaysia

*Corresponding author's email: aidafazliza@uitm.edu.my

Abstract

The undoped LiMn_2O_4 and doped $\text{LiMn}_{1.9}\text{Ti}_{0.095}\text{Sn}_{0.005}\text{O}_4$ materials were synthesized via sol-gel method and annealed at 700 °C for 24 hours. The structure and morphology of the materials were characterized using X-ray Powder Diffraction (XRD) and Field Emission Scanning Electron Microscopy (FESEM). The electrochemical performances of the materials were characterized by galvanostatic charge-discharge test in the voltage range of 2.5V-4.2V using a current of 1.0 mA. XRD results showed that the materials are pure and single phase with $Fd\bar{3}m$ space group. The $\text{LiMn}_{1.9}\text{Ti}_{0.095}\text{Sn}_{0.005}\text{O}_4$ material delivers a high initial capacity of 147.92 mAh g^{-1} with excellent cycleability compared to the undoped LiMn_2O_4 . The excellent capacity retention of $\text{LiMn}_{1.9}\text{Ti}_{0.095}\text{Sn}_{0.005}\text{O}_4$ material is largely due to the structural stabilization which results from the co-doping of titanium and tin in Mn. It implied doped with titanium and tin plays an important role to improve the cyclic stability and rate capacity of the lithium manganese oxides.

Keywords: Cathode; Li-ion battery; sol-gel; LiMn_2O_4 ; electrochemical performance

1.0 INTRODUCTION

Research in the field of rechargeable lithium-ion batteries has progressed tremendously in the past decade through an increasing demand for portable electronic devices, such as laptop computers and cellular phones, offering batteries with high energy density, flexible and light-weight as well as longer service life (Liu, Huang, Qian, Hy, Fang, Luo, & Meng, 2016).

The lithium cobaltate and lithium nickelate have successfully found a niche in this growing batteries market over the past decade. However, Co and Ni are toxic chemicals (Hong & Sun, 2002). To replace these cathode materials, other non-toxic, environmentally friendly and low cost materials with specific capacity close to that of the Co based batteries are under intensive studies. The lithium manganese spinel LiMn_2O_4 is a very attractive material. It possesses advantages such as non-toxic, good characteristics, environmentally friendly, abundantly found in nature and low cost with theoretical specific capacity of 148 mAh g^{-1} (Zhu, 2014). However, it displays a big disadvantage of premature capacity loss due to Jahn-Teller effect especially at high temperature (Xifei, Xu, & Wang, 2009).

One of the characteristics of manganese ion is that it can be easily replaced by either lithium ion or other transition metal ions (Hwang, Santhanam, & Hu, 2002). As such substitution of manganese ion with other transition metal is thought to be one of the way to improve this capacity fading. Titanium dioxide and Tin (II) oxide is a transition-metal and a post transition-metal respectively. Adding a small amount of 0.1-5.0 wt% of the titanium dioxide and tin (II) oxide is believed to increase the discharge capacity of the cell because of its function that is to stabilize the structure and improving rechargeability (Mieczkowska, 1994).

Many research groups are investigating this sol-gel method for use as a cathode material in micro and nano batteries. Sol-gel micro and nano batteries have been studied for various applications. To date, cathode electrode films are usually fabricated by sputtering, electron beam evaporation, and pulse-laser deposition. These methods, however, have several disadvantages such as difficulty in controlling the stoichiometry, long periods of deposition and high cost for fabrication (Cao & Prakash, 2002). So, sol-gel method is the only alternative approach to overcome these problems. This smart and brilliant method offers advantages such as excellent control of stoichiometry, easy control of crystallinity, density, and microstructure. Moreover, the fabrication cost is relatively much lower and the deposition rate is high. So in this work we proposed to use the sol-gel method because of its advantages over other methods.

2.0 METHODOLOGY

2.1 Synthesis by Sol-Gel Method

A stoichiometric proportion of high purity lithium acetate dehydrate $\leq 98\%$ (Sigma-Aldrich), manganese (II) acetate Tetrahydrate 99+ (Fluka Analytical), anatase Titanium (IV) oxide 99.8% (Aldrich Chemistry) and Tin (II) oxide 97% (Aldrich Chemistry) are dissolved in ethanol and homogeneously mixed using a magnetic stirrer for an hour. An equal volume of 1M aqueous solution of oxalic acid is added as a gelling agent in the solution until a thick, gel-like mixture is formed. In this case, maintaining the pH at 5.5 is very important as to standardize the pH level of the mixture. The mixture is then slow drying at around 100°-150°C until solvent has evaporated and a precursor material is formed. Using an agate mortar, the precursor is grinded into a very fine powder. The precursors are then annealed at high temperature of 700°C for 24 hours.

2.2 Characterization of the Samples

The effects of sol-gel route on all stoichiometries were measured by using X-ray Powder Diffraction (XRD) from PANalytical Xpert Pro, Field Emission Scanning Electron Microscopy (FESEM) by using JEOL JSM-7600F and charge-discharge test was done using a battery tester (WBCS 3000). The characterization and electrochemical test are described briefly in our previous work (Elong, Kamarulzaman, & Roshidah, 2016).

3.0 RESULTS AND DISCUSSION

The X-ray diffraction pattern (XRD) of undoped LiMn_2O_4 and doped $\text{LiMn}_{1.9}\text{Ti}_{0.095}\text{Sn}_{0.005}\text{O}_4$ annealed at 700 °C for 24 hours are shown in Figure 1. Both samples show a well-defined spinel structure without any impurity phases. This shows that Ti^+ and Sn^+ ion has successfully substituted in the parent LiMn_2O_4 structure. All diffraction lines can be indexed by using Miller

indexing method and it is agreed with the JCPDS indexing from the XRD. It can be clearly observed that the entire fingerprint peaks *viz* (111), (311), (222), (400), (331), (511), (440), (531), (533), (622), (444), and (711) are easily identifiable in all of the XRD patterns. All the diffraction peaks can be indexed with face centre cubic type structure based on spinel crystal system ($Fd\bar{3}m$ space group).

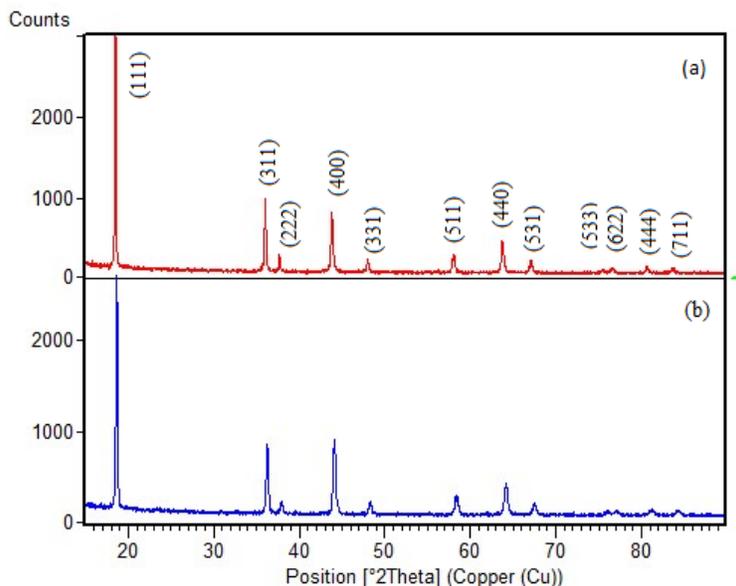


Figure 1 XRD patterns of samples (a) LiMn_2O_4 and (b) $\text{LiMn}_{1.9}\text{Ti}_{0.095}\text{Sn}_{0.005}\text{O}_4$ annealed at $700\text{ }^\circ\text{C}$ for 24 hours

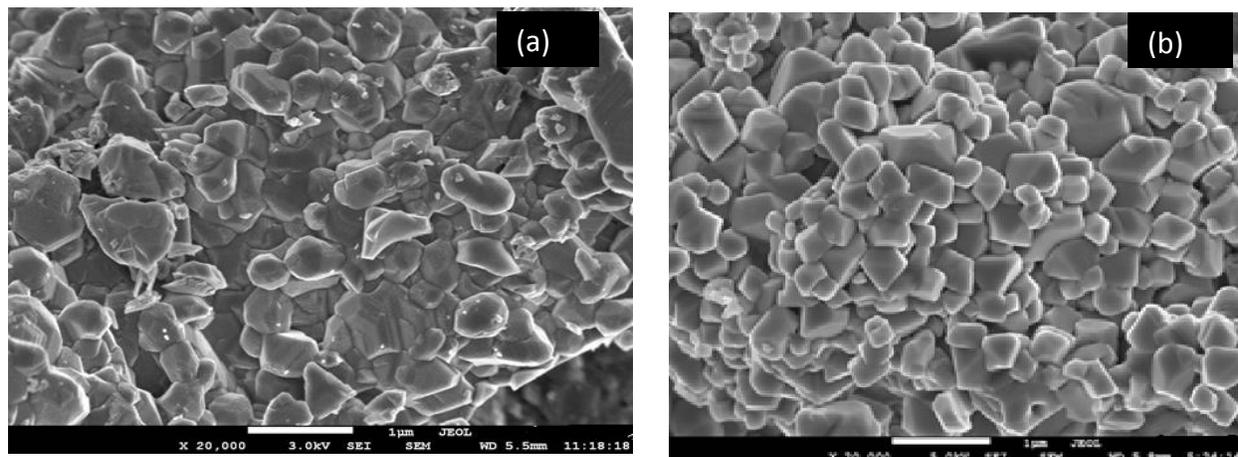


Figure 2 SEM images of samples (a) LiMn_2O_4 and (b) $\text{LiMn}_{1.9}\text{Ti}_{0.095}\text{Sn}_{0.005}\text{O}_4$ annealed at $700\text{ }^\circ\text{C}$ for 24 hours

The SEM images of LiMn_2O_4 and $\text{LiMn}_{1.9}\text{Ti}_{0.095}\text{Sn}_{0.005}\text{O}_4$ samples annealed at $700\text{ }^\circ\text{C}$ for 24 hours are displayed in Figure 2. It can be observed that for both samples, the grains consist of well-formed polyhedral particles existing in agglomerated form and of spherical-type crystallites. The crystallite size is

about 675nm for LiMn_2O_4 whereby for $\text{LiMn}_{1.9}\text{Ti}_{0.095}\text{Sn}_{0.005}\text{O}_4$ samples is around 325nm. The crystallite size was determined by measuring the average particle size from Figure 2 above. It shows that the crystallite size becomes smaller for doped samples and has sharper edges compared to the undoped samples.

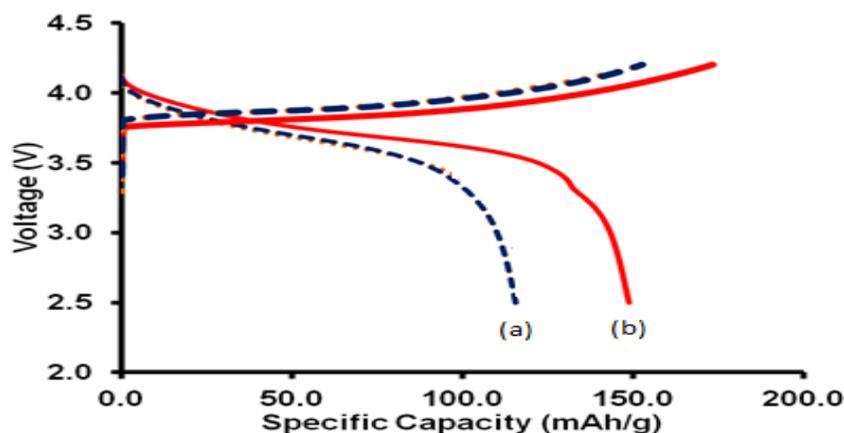


Figure 3a Initial charge-discharge curves for samples (a) LiMn_2O_4 and (b) $\text{LiMn}_{1.9}\text{Ti}_{0.095}\text{Sn}_{0.005}\text{O}_4$ annealed at 700 °C for 24 hours

The initial charge-discharge curves of samples LiMn_2O_4 and $\text{LiMn}_{1.9}\text{Ti}_{0.095}\text{Sn}_{0.005}\text{O}_4$ and its specific capacities of the cells are shown in Figure 3a. For LiMn_2O_4 and $\text{LiMn}_{1.9}\text{Ti}_{0.095}\text{Sn}_{0.005}\text{O}_4$ samples annealed at 700 °C for 24 hours, it can deliver an initial specific discharge capacity of 119.87 mAh g^{-1} and 147.92 mAh g^{-1} respectively. $\text{LiMn}_{1.9}\text{Ti}_{0.095}\text{Sn}_{0.005}\text{O}_4$ sample shows better capacity fading that is 21.39 % compared to LiMn_2O_4 sample where the capacity loss is a bit higher that is 49.90 % after 50th cycle. This can be observed from Figure 3b. $\text{LiMn}_{1.9}\text{Ti}_{0.095}\text{Sn}_{0.005}\text{O}_4$ sample shows better performance as it has smaller crystallite size. This is mainly due to the gelling agent used that is oxalic acid as it helps to reduce crystallite size in the compound (Liu et al. 2014). The excellent capacity retention of $\text{LiMn}_{1.9}\text{Ti}_{0.095}\text{Sn}_{0.005}\text{O}_4$ material is largely due to the structural stabilization which results from the co-doping of titanium and tin in Mn. Substitution doping of $\text{LiMn}_{1.9}\text{Ti}_{0.095}\text{Sn}_{0.005}\text{O}_4$ with Ti and Sn has improved the battery performance as well as improved cyclability compared to the standard LiMn_2O_4 .

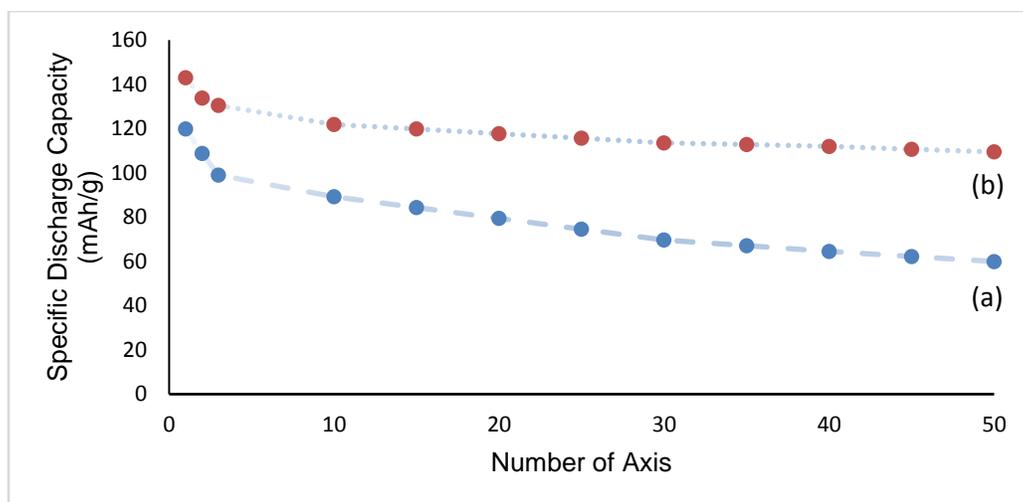


Figure 3b Cycling data of samples (a) LiMn_2O_4 and (b) $\text{LiMn}_{1.9}\text{Ti}_{0.095}\text{Sn}_{0.005}\text{O}_4$ annealed at $700\text{ }^\circ\text{C}$ for 24 hours

4.0 CONCLUSION

Substitution of Ti and Sn in spinel LiMn_2O_4 synthesized using the sol-gel method has been successfully done. $\text{LiMn}_{1.9}\text{Ti}_{0.095}\text{Sn}_{0.005}\text{O}_4$ material samples annealed at $700\text{ }^\circ\text{C}$ for 24 hours shows good and promising cathode material exhibiting an initial discharge capacity of 147.92 mAh g^{-1} and a capacity retention of more than 78% after 50th cycle.

Acknowledgements

The authors would like to thank the Institute of Science, UiTM Shah Alam, Malaysia for funding this project.

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